(54) **Components and catalysts for the polymerization of olefins**

Katalysator und Bestandteil für die Olefinpolymerisation

Composant et catalyseur pour polymérisation d'oléfines

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EP 0 395 083 B1

Description

This invention refers to catalyst components for the polymerization of olefins, the catalysts obtained from them.

Catalysts for the polymerization of olefins comprising a titanium halide supported on anhydrous magnesium halides in active form are described extensively in patent literature.

Patent literature has become abundant since the use of magnesium halides in active form as supports for Ziegler-Natta catalyst components was described for the first time in USA patents n. 4,298,718 and 4,495,338.

The most active forms of the magnesium halides are characterized by X-ray spectra where the maximum intensity reflection which appears in the spectrum of the nonactive halides is no longer present, but is substituted by a halo with the maximum intensity shifted towards the lower angles with respect to the one of the maximum intensity reflection in the nonactive halide.

In the less active forms of the magnesium chloride the maximum intensity reflection which appears at 2.56 Å (2 = ϑ 35°) is no longer present, but is substituted by a halo with a maximum intensity between the angles 2 ϑ of 33.5° and 35°; a reflection at 2 ϑ of 14.95° is always present.

The introduction in industrial practice of catalysts supported on magnesium chloride made possible significant simplifications to the polyolefin production processes. In particular, the possibility of obtaining catalysts in the form of spherical particles capable of producing polymers which duplicate the form of the catalyst, have satisfactory morphological characteristics (flowability and bulk density), and do not require granulation which, as is well known, is expensive in terms of energy use.

Examples of catalysts with controlled particle size are described in USP 3,953,414.

The polymer (polyethylene) which can be obtained with said catalysts has good morphological characteristics; the polymer productivity of these catalysts, however, is not very high (generally between 2,000 and 15,000 g/g catalyst). When the polymer yield rises to values higher than 20,000 g/g catalyst, the polymer particles formed are fragile and the apparent density is very low.

The catalyst components described in the above mentioned US patent are obtained from an $MgCl_2.6H_2O$ adduct spherulized in an apparatus of the dry cooling type, and then reacted with $TiCl_4$.

USP 4,399,054 describes catalyst components for the polymerization of olefins capable of producing polymer (polypropylene) with good flowability and bulk density characteristics. The polymer productivity of the catalyst is not very high (between 3,000 and 9,000 g/g catalyst; polymerization in heptane at 70°C for 4 h with partial propylene pressure of 7 atm.).

The catalyst components are obtained from $MgCl_2$ adducts with alcohols, in the form of spherical particles containing generally 3 moles of alcohol.

Before the reaction with $TiCl_4$ the alcohol content is lowered to 2.5-2 moles in order to render the catalysts suitable to obtain non-fragile spherical form polymers. The alcohol content is never lowered below the 2 moles (this reduces drastically the activity of the catalyst).

In the case of magnesium chloride, at least in the less active forms (those where in the spectrum are present two halos with intensity peaks respectively between 2 ϑ angles from 30.45° to 31°, and from 33.5° to 35°), the reflection that in the nonactive magnesium chloride spectrum appears at 2 ϑ of 14.95° is still present.

EP-A-65 700 discloses Ti-containing catalyst components prepared by reacting a Ti-halide with solid $MgCl_2$ particles showing a particular X-ray spectrum, which is the consequence of the particular spray drying process employed in the preparation of said particles. In the examples it is explained that after the reaction with the Ti-halide, the X-ray spectrum of the solid shows a peak at 10.8 Å (1 Å = 0.1 nm) corresponding to a 2ϑ angle of 8.18°, with no other peaks. The catalysts obtained from said catalyst components appear to be effective in the polymerization of ethylene only.

Catalyst components, for the polymerization of $CH_2=CHR$ olefins, where R is hydrogen or an alkyl or aryl radical with 1-8 carbon atoms have now been found, suitable to obtain catalysts capable of producing polymers in the form of sperical particles with optimum morphological characteristics (flowability and high bulk density). Moreover, the catalysts have a significant catalytic activity and stereospecifity.

The catalyst components of the invention are in the form of spherical particles having an average diameter between 10 and 350 μm , and comprise a titanium compound containing at least a Ti-halogen link, and optionally an electron-donor compound, supported on magnesium chloride. They are characterized by a surface area between 20 and 250 m^2/g, porosity greater than 0.2 cc/g (1 cc = 1 cm^3) and preferably comprised between 0.2 and 0.5 cc/g, X-ray spectrum (CuKα) where

a) reflections at 2 ϑ of 35° and 14.95° (characteristic of magnesium chloride) are present, or

b) where the reflection at 2 ϑ of 35° is substituted by a halo with a maximum intensity between the 2 ϑ angles of 33.5° and 35°, and the reflection at 2 ϑ of 14.95° is not present.

For the definition of the X-ray spectrum of magnesium chloride, reference is made to the standard ASTM D-3854.

The registration of the spectrum is done using a copper anti-cathode and K α radiation.

· The spectrum with the a) characteristic is peculiar of the catalytic components with surface area smaller than 70-80 m^2/g and porosity greater than 0.4 cc/g. The spectrum with the b) characteristic is given by components with an area greater than 60 m^2/g and porosity between 0.25 and 0.4 cc/g.

5 The pore volume distribution is such that more than 50% of the pores have a radius greater than 100 Å. In the components with area smaller than 100 m^2/g, more than 70% of the pores have a radius greater than 100 Å.

As already indicated, the catalyst components of the invention supply catalysts suitable for the production of olefins (co)polymers in the form of spherical particles with valued morphologic characteristics (high bulk density values, flow-ability, and mechanical resistance). The average diameter of the polymeric particles is between 50 and 5000 μm.

10 In particular, catalysts obtained from components with surface area smaller than 100 m^2/g and a porosity greater than 0.4 cc/g, are appropriately used in the preparation of ethylene polymers (HDPE and LLDPE). The catalysts have a very high activity and the spherical polymer obtained has attractive morphological characteristics (very high bulk density, flowability and mechanical resistance).

The catalysts obtained from components with surface area greater than 60-70 m^2/g and porosity smaller than 0.4 15 cc/g are preferred for use in preparing crystalline propylene homo and copolymers, the so called impact copolymers obtained with sequential polymerization of 1) propylene, and 2) ethylene-propylene mixtures.

They are also advantageously used in the preparation of ethylene-propylene rubbers (EP rubbers), or ethylene-propylene-diene rubbers (EPDM rubbers), and of propylene polymer compositions which contain said rubbers.

It is surprising that with the catalysts of this invention said types of rubber in spherical particles with good flowability 20 and bulk density characteristics can be obtained, because up to now it has not been possible to prepare elastomeric polymers of the above indicated type in flowable granular particles due to the insurmountable problems of the fouling of the reactors and/or the agglomeration of the particles.

It is also surprising that the catalysts of the invention are highly active although the magnesium chloride in them gives X-ray spectra characteristic of the low active forms of the magnesium chloride itself.

25 Finally it is surprising and completely unexpected that the magnesium chloride is present in the crystalline form with an X-ray spectrum as the one indicated in b).

The preparation of the catalyst components is carried out in a variety of ways. The preferred method consists in starting with magnesium chloride/alcohol adducts containing alcohol moles in such a number that the adduct is solid at room temperature, but melted at temperatures between 100-130°C.

30 The number of alcohol moles vary with the different types of alcohol.

The alcohols suitable for use have the ROH formula where R is an alkyl, cycloalkyl, or aryl radical with 1-12 carbon atoms. It is also possible to use mixtures of said alcohols.

Examples of alcohols are methanol, ethanol, propanol, butanol, 2-ethylhexanol and their mixtures.

With alcohols such as ethanol, propanol, and butanol, the number of moles is about 3 per $MgCl_2$ moles. The alcohol 35 and the magnesium chloride are mixed in an inert hydrocarbon liquid immiscible with the adduct, brought to the fusion temperature of the adduct. The mixture undergoes vigorous stirring [using for example an ULTRA TURRAX T-45N apparatus rotating at 2000-5000 RPM (Jonke & Kunkel K.G.IKG Werkel)].

The emulsion obtained is cooled in a very short time. This causes the solidification of the adduct in the form of spherical particles with the desired dimensions. The particles are dried and then subjected to a partial dealcoholation 40 by heating it to temperatures going from 50° to 130°C.

The partially dealcoholated adduct is in the form of sperical particles with an average diameter between 50 and 350 μm, a surface area between 10 and 50 m^2/g and porosity from 0.6 to 2 cc/g (determined with a mercury porosimeter).

The higher the degree of dealcoholation, the higher the porosity. The pore volume distribution is such that more 45 than 50% of the pores have a radius greater than 10,000 A.

The dealcoholation is carried out until the alcohol contents are not greater than 2 moles per $MgCl_2$ mole, preferably comprised between 0.15 and 1.5 moles, particularly between 0.3 and 1.5 moles.

Whenever the dealcoholation is brought to values lower than 0.2 alcohol moles per $MgCl_2$ mole, the catalytic activity is considerably reduced.

50 The partially dealcoholated adduct is then suspended in cold $TiCl_4$ at a concentration of 40-50 g/l, and then brought to a temperature of 80°-135°C and maintained at said temperature for 0.5-2 hrs. The excess $TiCl_4$ is separated hot via filtration or sedimentation.

The treatment with $TiCl_4$ is repeated one or more times if the alcohol content desired should be very low (generally less than 0.5% by weight).

55 During the preparation of a catalytic component containing an electron-donor compound, the latter is added to the $TiCl_4$ in quantities equal to molar ratios with respect to $MgCl_2$ between 1:6 and 1:16.

After the treatment with $TiCl_4$, the solid is washed with a hydrocarbon (e.g. hexane or heptane) and then dried.

According to another method, the melted adduct while in emulsion in an inert hydrocarbon is passed through a

tube of the proper length under turbulent motion and then gathered in an inert hydrocarbon maintained at low temperature. Said method is described in USP n. 4,399,054. In this case as well the particles of the adduct are subjected to partial dealcoholization and reaction with $TiCl_4$.

As a variant to the methods described above the titanium compound, especially when it is solid at room temperature
5 such as for instance the $TiCl_3$, is dissolved in the melted adduct which is then dealcoholated as indicated above and subjected to a reaction with a halogenating agent capable of reacting and separating the hydroxylic groups, such as for instance $SiCl_4$.

In the starting melted adduct, besides the titanium compound and optionally other transition metals, also co-supports such as $AlCl_3$, $AlBr_3$, $ZnCl_2$ may be included.
10 The titanium compounds suitable for the preparation of catalyst components, besides $TiCl_4$ and $TiCl_3$ and similar halides, also include other compounds with at least one Ti-halogen link, such as halogen alcoholates like trichlorophenoxytitanium and trichlorobutoxytitanium.

Finally the titanium compound can be used in mixtures with other transition metal compounds, such as V, Zr and Hf halides and halogen alcoholates.
15 As already indicated, the catalyst component may also contain an electron-donor compound (internal donor). This is necessary when the catalyst component must be used in the stereoregular polymerization of olefins such as propylene, 1-butene and 4-methyl-1-pentene.

The electron-donor compounds can be selected among compounds including ethers, esters, amines, ketons.

Preferred compounds are the alkyl esters, cycloalkyls and aryls of polycarboxyl acids, such as phthalic and maleic
20 acids, and ethers of the formula
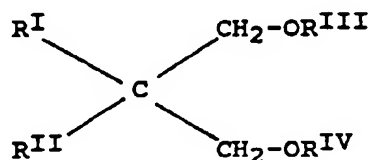
$$R^{I} \diagdown \diagup CH_2\text{-}OR^{III}$$
$$C$$
$$R^{II} \diagup \diagdown CH_2\text{-}OR^{IV}$$

30 where R^I, R^{II}, same or different from each other, are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms; R^{III} and R^{IV}, same or different, are alkyl radicals with 1-4 carbon atoms.

Ethers of this type are described in EP-A-344 755.

Examples representing said compounds are n-butyl phthalate, diisobutyl phthalate, di-n-octyl phthalate, 2-methyl-2 methyl-2-isopropyl-1,3-dimethoxypropane; 2-methyl-2-isobutyl-1,3-dimethoxypropane,2,2-diisobutyl-1,3-dimethox-
35 ypropane, 2-isopropyl-2-isopentyl-1,3-dimethoxypropane.

The internal donor is generally present in molar ratios with respect to Mg of 1:8-1:14. The titanium compound expressed as Ti is present in a percentage between 0.5 and 10% by weight.

Al-alkyl compounds selected particularly among Altrialkyls, such as Al-triethyl, Al-triisobutyl and Al-tri-n-butyl, are used as co-catalysts.
40 The Al/Ti ratio is greater than 1 and is generally between 20-800.

In case of stereoregular polymerization of alpha olefins such as propylene and 1-butene, besides the Al-alkyl compound, usually, also an electron-donor compound (external donor is used). This compound may be the same as or different from the electron-donor compound present as internal donor.

When the internal donor is an ester of a polycarboxylic acid, especially a phthalate, the external donor is preferably
45 selected among the silicon compounds of the formula $R_1R_2Si(OR)_2$, where R_1 and R_2 are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms, and R is an alkyl radical with 1-4 carbon atoms. Examples representing these silanes are methyl cyclohexyl dimethoxysilane, diphenyl dimethoxysilane, methyl-t.butyl dimethoxysilane.

1,3-diethers with the formula previously shown may also be used advantageously. .

If the internal donor is one of these diethers, there is no need to use an external donor, since the stereospecifity
50 of the catalyst is in itself sufficiently high.

Catalysts containing an internal donor are used in the preparation of LLDPE with restricted molecular weight distribution. As already indicated, the catalysts are used in the polymerization of $CH_2=CHR$ olefins where R is a hydrogen, or an alkyl or aryl radical with 1-8 carbon atoms, and mixtures of said olefins with or without a diene.

The polymerization is done according to known methods operating in liquid phase, in the presence or absence of
55 an inert hydrocarbon diluent, or in gaseous phase.

It is also possible to use liquid-gas mixed processes where in one or more stages the polymerization is carried out in liquid phase, and in one or more successive stages it is carried out in gaseous phase.

The polymerization temperatures are in general between 20° and 150°C, preferably between 60° and 90°C. The

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operation takes place at atmospheric pressure or higher.

The data shown in examples and text relative to the following properties have been determined according to the methods indicated below.

Property	Method
- MIL flow index	ASTM-D 1238
- MIE " "	ASTM-D 1238
- MIF " "	ASTM-D 1238
- Fraction soluble in xylene	(see Determination before Examples)
- Isotacticity Index (I.I.)	Weight percentage of polymer insoluble in xylene at 25°C. Basically it conforms with the weight percentage of polymer insoluble in boiling n-heptane)
- Surface area	B.E.T. (apparatus used SORPTOMATIC 1800 - C. Erba).
- Porosity	Unless otherwise indicated, the porosity is determined with the B.E.T. method (see above). It is calculated from the integral pore distribution curve in function of the pores themselves.
- Porosity (mercury)	Determined by immersing a known quantity of the sample in a known quantity of mercury inside a dilatometer and gradually hydraulically increasing the pressure of the mercury. The pressure of introduction of the mercury in the pores is in function of the diameter of same. The measurement is done using a porosimeter "Porosimeter 2000 Series" (C. Erba). The total porosity is calculated from the volume decrease of the mercury and the values of the pressure applied.
- Bulk density	DIN-53194
- Flowability	The time taken by 100 g of polymer to flow through a funnel with an output hole of a diameter of 1.25 cm, and walls with an inclination of 20° on the vertical.
- Morphology	ASTM-D 1921-63

Determination of percentage in soluble xylene

2 g of polymer are dissolved in 250 ml of xylene at 135°C while agitating. After 20 minutes the solution is left to cool, still under agitation, until it reaches 25°C.

After 30 minutes the precipitated material is filtered through filter paper; the solution is evaporated in nitrogen current and the residue is dried under vacuum at 80°C until it reaches constant weight.

Thus the percentage of polymer soluble in xylene at room temperature is calculated.

EXAMPLES

PREPARATION OF MgCl$_2$/ALCOHOL ADDUCTS.

The MgCl$_2$/alcohol adducts in spherical particle form are prepared following the method described in example 2 of USP n. 4,399,054, but operating at 3,000 RPM instead of 10,000 RPM.

The adduct was partially dealcoholated by heat at increasing temperatures from 30°C to 180°C operating in nitrogen current.

PREPARATION OF THE SOLID CATALYST COMPONENT.

In a 1 litre flask equipped with a condenser and mechanical agitator were introduced, under a nitrogen current, 625 ml of TiCl$_4$. At 0°C while agitating were added 25 g of partially dealcoholated adduct. It was then heated up to 100°C in 1 hour, when the temperature reaches 40°C diisobutylphthalate (DIBF) was added in molar ratio Mg/DIBF=8.

The temperature was maintained at 100°C for 2 hours, it was then left to decant and afterwards the hot liquid was syphoned off. 550 ml of TiCl$_4$ were added and it was heated to 120°C for 1 hour. Finally it was left to settle and the liquid was syphoned off while hot; the residual solid was washed 6 times with 200 ml aliquote of anhydrous hexane at 60°C and 3 times at room temperature.

The solid was then dried under vacuum.

POLYMERIZATION OF PROPYLENE

In a 4 l stainless steel autoclave equipped with an agitator and a thermostatic system, which had been degassed with nitrogen at 70°C for 1 hour and then with propylene, was introduced at 30°C without agitation but under light propylene flow, the catalytic system consisting of a suspension of the above solid catalyst component in 80 ml of hexane, 0.76 g of Al-triethyl and 8.1 mg of diphenyldimethoxysilane (DPMS). The suspension was prepared immediately prior to the test.

The autoclave was then closed and 1 Nl of H_2 was introduced. While agitating 1.2 kg of liquid propylene were charged and the temperature was brought to 70°C in five minutes, maintaining the value constant for 2 hours.

At the end of the test, the agitation was stopped and any unreacted propylene was removed. Once the autoclave was cooled to room temperature, the polymer was recovered and then dried at 70°C under nitrogen current in oven for 3 hours and then analyzed.

COPOLYMERIZATION OF ETHYLENE WITH BUTENE-1 (LLDPE)

The autoclave described above was degassed with propane instead of propylene. The catalytic system consisting of 25 cc of hexane, 1.05 g of Al-triisobutyl and the above catalyst component, was introduced in the autoclave at room temperature under light propane flow. The pressure was increased to 5.5 bar (5.5 atm.) with H_2 and then to 2 bar (2 atm.) with ethylene, prepolymerizing the ethylene until 15 g of ethylene were used (45°C).

The propane and the hydrogen were degassed and after washing with H_2 the gaseous phase was formed with 37.0 g of ethylene, 31.9 g of butene-1, and 1.8 bar (1.8 atm.) of H_2 (total pressure 15 bar (15 atm.)).

An ethylene-butene-1 mixture was then fed in a weight ratio of 9:1 at 70°C for 2 hours

At the end the autoclave was degassed and cooled rapidly to room temperature.

The recovered copolymer was dried at 70°C in nitrogen for 4 hours in an oven.

POLYMERIZATION OF ETHYLENE

A 2.5 l stainless steel autoclave equipped with agitator and thermostatic system was flushed as described above for the test with propylene but using ethylene instead of propylene.

At 45°C were introduced in H_2 current, 900 ml of a solution containing 0.5 g/l of Al-triisobutyl in anhydrous hexane and immediately afterwards, the catalyst component suspended in 100 ml of the above mentioned solution.

The temperature was rapidly brought to 70°C and H_2 was fed until the pressure reached 3 bar (3 atm.), then ethylene up to 10.5 bar (10.5 atm.). These conditions were maintained for 3 hours replenishing continuously the ethylene depleted. At the end of the polymerization reaction, the autoclave was rapidly vented and cooled at room temperature.

The polymeric suspension was filtered and the solid residue dried in nitrogen at 60°C for 8 hours.

Example 1

A spherical $MgCl_2.3EtOH$ adduct (obtained as indicated in the general method) was dealcoholated until an $EtOH/MgCl_2$ molar ratio of 1.7 was obtained.

A product with the following characteristics was obtained:

- porosity (mercury) = 0.904 cc/g;
- surface area = 9.2 m^2/g;
- bulk density = 0.607 g/cc.

From this adduct, through the $TiCl_4$ treatment described in the general method, a solid catalyst component in spherical form was obtained with the following characteristics:

- Ti = 2.5% by weight;
- DIBF = 8.2% by weight;
- porosity = 0.405 cc/g;
- surface area = 249 m^2/g;
- bulk density = 0.554 g/cc.

The X-ray spectrum of this component did not have reflections at 2 ϑ of 14.95°; a halo with a maximum intensity of 2 ϑ of 34.72° was present instead.

This catalyst component was used in the polymerization of propylene following the technique described in the general section. Using 0.01 g of component 430 g of polymer were obtained with the following characteristics:

- fraction soluble in xylene at 25°C = 2.4%;
- MIL = 2.5 g/10';
- bulk density = 0.48 g/cc;
- morphology: 100% spherical particles with diameter between 1000 and 5000 μm ;
- flowability: 10 sec.

Example 2

By partially dealcoholating (according to example 1) a $MgCl_2.3EtOH$ spherical adduct also obtained according to the method indicated in example 1, an adduct was prepared with an $EtOH/MgCl_2$ molar ratio of 1.5, and with the following characteristics:

- porosity (mercury) = 0.946 cc/g;
- surface area = 9.1 m^2/g;
- bulk density = 0.564 g/cc.

From this adduct, through $TiCl_4$ treatment as indicated above, a spherical catalyst component was prepared with the following characteristics:

- Ti = 2.5% weight;
- DIBF = 8.0% weight;
- porosity = 0.389 cc/g;
- surface area = 221 m^2/g;
- bulk density = 0.555 g/cc.

The X-ray spectrum of the component did not show reflections at 2 ϑ of 14.95°; only a halo was present with a maximum intensity at 2 ϑ of 2.5780°.

This catalyst component was used in the polymerization of the propylene using the procedure of example 1.

Using 0.015 g of catalyst component, 378 g of polypropylene were obtained with the following characteristics:

- fraction soluble in xylene at 25°C = 2.6%;
- MIL - 2.8 g/10';
- bulk density = 0.395 g/cc;
- morphology = 100% spherical particles with diameter between 1000 and 5000 μm;
- flowability - 12 sec.

Example 3

By partially dealcoholating (according to example 1) a $MgCl_2.3EtOH$ spherical adduct obtained according to the method indicated in the preceding examples, an $EtOH/MgCl_2$ = 1 adduct was obtained which has the following characteristics:

- porosity (mercury) = 1.208 cc/g;
- surface area = 11.5 m^2/g;
- bulk density = 0.535 g/cc.

From said adduct, through $TiCl_4$ reaction, following the methodology described in the preceding examples, was obtained a spherical catalytic component with the following characteristics:

- Ti = 2.2% weight;
- DIBF = 6.8% weight;
- porosity = 0.261 cc/g;
- surface area = 66.5 m^2/g;
- apparent density = 0.440 g/cc.

The X-ray spectrum of the catalytic component showed a reflection at 2 ϑ of 14.95° as well as one at 2 ϑ = 35°.
Using 0.023 g of the catalyst component in the propylene polymerization using the conditions in example 1, 412 g of polypropylene were obtained with the following characteristics:

- fraction soluble in xylene at room temperature = 3.0%;
- MIL - 3.2 g/10';
- bulk density = 0.35 g/cc;
- morphology = 100% spherical particles with diameter between 500 and 5000 μm ;
- flowability - 12 sec.

Following the previous general description of the procedure for the copolymerization of ethylene with butene, 0.0238 g of catalyst component were used and 240 g of copolymer was obtained with the following characteristics:

- linked butene = 8.3% weight;
- fraction soluble in xylene at room temperature = 12.2%;
- MIE = 12 g/10';
- MIF = 12 g/10';
- MIF/MIE = 30;
- morphology = 100% spherical particles with diameter between 500 and 5000 μm.

Example 4

By partially dealcoholating (according to example 1) a $MgCl_2.3EtOH$ spherical adduct obtained according to the method indicated in the preceding examples, an EtOH/Mg = 0.4 adduct was obtained which had the following characteristics:

- porosity (mercury) = 1.604 cc/g;
- surface area = 36.3 m^2/g;
- apparent density = 0.410 g/cc.

By treating this support with $TiCl_4$ at a temperature of 135°C, at a concentration of 50 g/l, with three 1 hour treatments, a spherical catalyst component was obtained which, after the elimination of the excess $TiCl_4$, washing and drying, had the following characteristics:

- Ti = 2.6% weight;
- porosity = 0.427 cc/g;
- surface area 66.5 m^2/g.

The X-ray spectrum of this component showed a reflection at 2 ϑ of 14.95° as well as at 2 ϑ of 35°.
Using 0.012 g of catalyst component in the polymerization of ethylene according to the method described in the general section, 400 g of polyethylene were obtained with the following characteristics:

- MIE = 0.144 g/10';
- MIF = 8.87 g/10';
- MIF/MIE = 61.6
- morphology = 100% spherical particles with diameter between 1000 and 5000 μm ;
- flowability = 12 sec.;
- apparent density = 0.38 g/cc.

Example 5

By partially dealcoholating (as per example 1) a $MgCl_2.3EtOH$ spherical adduct obtained according to the method indicated in the preceding examples, an adduct was obtained with EtOH/$MgCl_2$ molar ratio of 0.15 with the following characteristics:

- porosity (mercury) = 1.613 cc/g;
- surface area = 22.2 m^2/g.

The X-ray spectrum of this component showed a reflection at 2 ϑ of 14.95° as well as 2 ϑ of 35°.

Using 0.03 g of this component in the polymerization of ethylene, as described in example 4, 380 g of polyethylene were obtained with the following characteristics:

- MIE = 0.205 g/10';
- MIF = 16.42 g/10';
- MIF/MIE = 80.1;
- flowability = 12 sec.;
- bulk density = 0.40 g/cc.

Example 6

A $MgCl_2.1EtOH$ adduct was prepared according to the method in example 3, but using also a quantity of water diluted in the alcohol used for the preparation of the starting $MgCl_2.3EtOH$ equal to 2% in weight.

The adduct after dealcoholation contained 3% in weight of water. With said adduct, after treatment with $TiCl_4$ and DIBF as described in example 1, a spherical catalyst component was obtained with the following weight composition:

- Ti = 2.35%;
- DIBF = 6.9%.

Using 0.025 g of this component in the polymerization of propylene as per example 1, 410 g of polymer in spherical particle form were obtained which had the following characteristics:

- fraction soluble in xylene at 25°C = 3.1%;
- MIL = 3.0 10';
- apparent density = 0.35 g/cc;
- morphology = 100% of the spherical particles having a diameter between 100 and 5000 μm ;
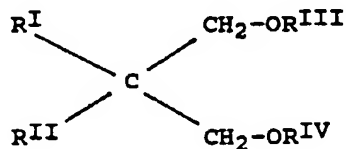- flowability = 13 sec.

Claims

1. A catalyst component for the polymerization of olefins comprising a titanium compound containing at least one Ti-halogen link supported on anhydrous magnesium chloride, said component being in the form of spherical particles with an average diameter between 10 and 350 μm , surface area between 20 and 250 m^2/g, porosity greater than 0.2 cc/g, having an X-ray spectrum where a) reflections at angle 2 ϑ of 35° and 2 ϑ of 14.95° are present, or b) where the reflection at 2 ϑ angle of 35° is no longer present but is substituted by a halo with a maximum intensity between angles 2 ϑ of 33.5° and 35°, and the reflection at angle 2 ϑ of 14.95° is not present.

2. The component of claim 1, further comprising an electron-donor compound in molar ratio with the magnesium chloride between 1:4 and 1:20.

3. The component of claim 1 or 2, where the surface area is less than 100 m^2/g, the porosity is greater than 0.44 cc/g and having an X-ray spectrum of the type a).

4. The component of claim 1 or 2, where the area is greater than 60 m^2/g, the porosity is between 0.2 and 0.4 cc/g, and having an X-ray spectrum of the type b).

5. The component of one or more of the preceding claims, where the pore volume distribution is such that at least 50% of them have a radius greater than 100 Å.

6. The component of one or more of the preceding claims, where the titanium compound is $TiCl_4$.

7. The component of one or more of claims 2 to 6, where the electron-donor compound is selected among alkyl, cycloalkyl, or aryl esters of phthalic acid.

8. The component of one or more of claims 2 to 6, where the electron-donor compound is selected among 1,3-diethers of the formula:

$$\begin{array}{c} R^{I} \diagdown \qquad \diagup CH_2\text{-}OR^{III} \\ C \\ R^{II} \diagup \qquad \diagdown CH_2\text{-}OR^{IV} \end{array}$$
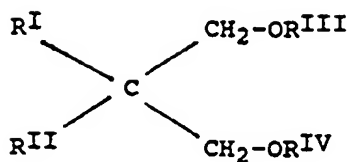
where R^I, R^{II}, same or different from each other, are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms, R^{III} and R^{IV}, same or different, are alkyl radicals with 1-4 carbon atoms.

9. The component of one or more of the preceding claims, where the titanium compound is present in quantity between 0.5% and 10% in weight, expressed as metallic Ti.

10. A catalyst for the polymerization of olefins, comprising the product of the reaction between a catalyst component of claim 1, and an Al-trialkyl compound.

11. The catalyst of claim 10, where an electron-donor compound (external donor) is used in the preparation of the catalyst.

12. The catalyst of claim 11, where the solid catalyst component includes an electron-donor selected among alkyl, cycloalkyl and aryl esters of phthalic acid, and the external donor is selected among silicon compounds of the formula $R_1R_2Si(OR)_2$, where R_1 and R_2 equal or different are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms, and R is an alkyl radical with 1-4 carbon atoms.

13. The catalyst of claim 11, where the external donor is selected among 1,3-diethers of the formula:

$$\begin{array}{c} R^{I} \diagdown \qquad \diagup CH_2\text{-}OR^{III} \\ C \\ R^{II} \diagup \qquad \diagdown CH_2\text{-}OR^{IV} \end{array}$$

where R^I, R^{II}, same or different from each other, are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms; and R^{III} and R^{IV}, same or different, are alkyl radicals with 1-4 carbon atoms.

14. A $MgCl_2$/ROH alcohol adduct, where R is an alkyl, cycloalkyl or alkylaryl radical with 1-12 carbon atoms, suitable for the preparation of the catalyst component of one or more of claims 1 to 9, containing from 0.2 to 2 moles of alcohol per mole of $MgCl_2$, and having a surface area between 10 and 50 m^2/g, porosity (mercury) from 0.6 to 2.5 cc/g and pore volume distribution such that at least 50% of the pores have a radius greater than 10,000 Å.

15. A process for preparing the catalyst component of one or more of the preceding claims 1 to 9, comprising reacting

1) the $MgCl_2$/ROH alcohol adduct of claim 14 with
2) a titanium compound containing at least one halogen-titanium bond.

Patentansprüche

1. Katalysatorkomponente zur Polymerisation von Olefinen, umfassend eine Titanverbindung, die zumindest eine Ti-Halogenbindung enthält und trägergestützt ist auf einem wasserfreien Magnesiumchlorid, wobei diese Komponente vorliegt in Form von sphärischen Teilchen mit einem durchschnittlichen Durchmesser zwischen 10 und 350 µm, einer spezifischen Oberfläche zwischen 20 und 250 m^2/g, einer Porosität von größer als 0,2 cm^3/g und ein Röntgenspektrum aufweist, worin a) Reflexionen bei dem Winkel 2 ϑ von 35° und 2 ϑ von 14,95° vorhanden sind, oder b) worin die Reflexion bei dem 2ϑ-Winkel von 35° nicht mehr vorhanden ist, sondern ersetzt ist durch einen Halo mit einer maximalen Intensität zwischen den Winkeln 2ϑ von 33,5° und 35° und die Reflexion bei dem Winkel

2 ϑ von 14,95° nicht vorhanden ist.

2. Komponente gemäß Anspruch 1, zusätzlich umfassend eine Elektronen-Donor-Verbindung in einem Molverhältnis zu dem Magnesiumchlorid zwischen 1:4 und 1:20.

3. Komponente gemäß Anspruch 1 oder 2, worin die spezifische Oberfläche geringer als 100 m²/g ist, die Porosität höher als 0,44 cm³/g ist;und die ein Röntgenspektrum des Typs a) aufweist.

4. Komponente gemäß Anspruch 1 oder 2, worin die spezifische Oberfläche größer als 60 m²/g ist, die Porosität zwischen 0,2 und 0,4 cm³/g ist, und die ein Röntgenspektrum des Typs b) aufweist.

5. Komponente gemäß einem oder mehreren der vorhergehenden Ansprüche, worin die Porenvolumenverteilung derart ist, daß zumindest 50% derselben einen Radius von größer als 100 Å besitzen.

6. Komponente gemäß einem oder mehreren der vorhergehenden Ansprüche, worin die Titanverbindung $TiCl_4$ ist.

7. Komponente gemäß einem oder mehreren der Ansprüche 2 bis 6, worin die Elektronen-Donor-Verbindung unter Alkyl-, Cycloalkyl- oder Arylestern der Phthalsäure ausgewählt ist.

8. Komponente gemäß einem oder mehreren der Ansprüche 2 bis 6, worin die Elektronen-Donor-Verbindung ausgewählt ist unter 1,5-Diethern der Formel
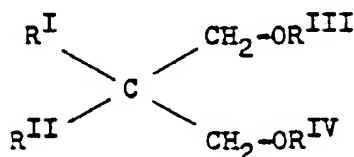
$$R^{I} \diagdown \diagup CH_2\text{-}OR^{III}$$
$$\phantom{R^{I}} C$$
$$R^{II} \diagup \diagdown CH_2\text{-}OR^{IV}$$

worin R^I und R^{II}, die gleich oder voneinander verschieden sind, Alkyl-, Cycloalkyl- oder Arylreste mit 1 bis 18 Kohlenstoffatomen bedeuten, R^{III} und R^{IV}, die gleich oder voneinander verschieden, Alkylreste mit 1 bis 4 Kohlenstoffatomen sind.

9. Komponente gemäß einem oder mehreren der vorhergehenden Ansprüche, worin die Titanverbindung in einer Menge zwischen 0,5 und 10 Gew.%, ausgedrückt als metallisches Ti, vorhanden ist.

10. Katalysator zur Polymerisation von Olefinen, umfassend das Reaktionsprodukt zwischen einer Katalysatorkomponente gemäß Anspruch 1 und einer Al-trialkylverbindung.

11. Katalysator gemäß Anspruch 10, worin eine Elektronen-Donor-Verbindung (äußerer Donor) bei der Herstellung des Katalysators verwendet wird.

12. Katalysator gemäß Anspruch 11, worin die feste Katalysatorkomponente einen Elektronen-Donor umfaßt, ausgewählt unter Alkyl-, Cycloalkyl- und Arylestern der Phthalsäure, und der äußere Donor ausgewählt ist unter Siliciumverbindungen der Formel $R_1R_2Si(OR)_2$, worin R_1 und R_2, die gleich oder voneinander verschieden sind, Alkyl-, Cycloalkyl- oder Arylreste mit 1 bis 18 Kohlenstoffatomen bedeuten und R für einen Alkylrest mit 1 bis 4 Kohlenstoffatomen steht.

13. Katalysator gemäß Anspruch 11, worin der äußere Donor ausgewählt ist unter 1,5-Diethern der Formel
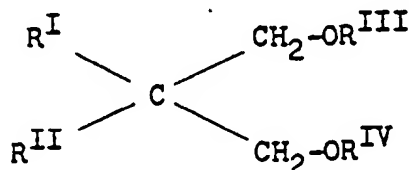
$$R^{I} \diagdown \diagup CH_2\text{-}OR^{III}$$
$$\phantom{R^{I}} C$$
$$R^{II} \diagup \diagdown CH_2\text{-}OR^{IV}$$

worin R^I und R^{II}, die gleich oder voneinander verschieden sind, Alkyl-, Cycloalkyl- oder Arylreste mit 1 bis 18 Kohlenstoffatomen bedeuten und R^{III} und R^{IV}, die gleich oder voneinander verschieden sind, Alkylreste mit 1 bis 4 Kohlenstoffatomen sind.

14. MgCl$_2$/ROH-Altoholaddukt, worin R einen Alkyl-, Cycloalkyl- oder Alkylarylrest mit 1 bis 12 Kohlenstoffatomen bedeutet, geeignet zur Herstellung der Katalysatorkomponente gemäß einem oder mehreren der Ansprüche bis 9, enthaltend 0,2 bis 2 Mol Alkohol je Mol MgCl$_2$ und mit einer spezifischen Oberfläche zwischen 10 und 50 m^2/g, einer Porosität (Quecksilber) von 0,6 bis 2,5 cm^3/g und einer Porenvolumenverteilung derart, daß zumindest 50% der Poren einen Radius von größer als 10 000 Å aufweisen.

15. Verfahren zur Herstellung der Katalysatorkomponente gemäß einem oder mehreren der vorhergehenden Ansprüche 1 bis 9, umfassend die Umsetzung

1) des MgCl$_2$/ROH-Alkoholaddukts gemäß Anspruch 14 mit
2) einer Titanverbindung, die zumindest eine Halogentitanbindung enthält.

Revendications

1. Un composant catalytique pour la polymérisation d'oléfines comprenant un dérivé de titane, contenant au moins une liaison Ti-halogène, supporté sur chlorure de magnésium anhydre, ledit composant étant sous la forme de particules sphériques présentant:

- un diamètre moyen compris entre 10 et 350 µm, une surface spécifique comprise entre 20 et 250 m^2/g,
- une porosité supérieure à 0,2 cm^3/g,
- un spectre aux rayons X où

a) les réflexions à l'angle 2θ de 35° et 2θ de 14,95 sont présentes, ou
b) la réflexion à l'angle 2θ de 35° n'est plus présente, mais est remplacée par un halo présentant une intensité maximum comprise entre les angles 2θ de 33,5° et 35° et la réflexion à l'angle 2θ de 14,95° n'est pas présente.

2. Le composant selon la revendication 1, comprenant en outre un dérivé électro-donneur dont le rapport molaire au chlorure de magnésium est compris entre 1/4 et 1/20.

3. Le composant selon les revendications 1 ou 2, où la surface spécifique est inférieure à 100 m^2/g, la porosité est supérieure à 0,44 cm^3/g et qui présente un spectre de rayons X du type a).

4. Le composant selon l'une quelconque des revendications 1 ou 2, dans lequel la surface est supérieure à 60 m^2/g, la porosité est comprise entre 0.2 et 0,4 cm^3/g, et qui présente un spectre aux rayons X du type b).

5. Le composant selon une ou plusieurs des revendications précédentes, dans lequel la distribution du volume de pores est tel qu'au moins 50% de ceux-ci ont un rayon supérieur à 100 Å.

6. Le composant selon une ou plusieurs des revendications précédentes dans lequel le dérivé de titane est TiCl$_4$.

7. Le composant selon une ou plusieurs des revendications 2 à 6, dans lequel le dérivé électro-donneur est choisi parmi les esters d'alkyle, de cyclo-alkyle ou d'aryle de l'oxyde phtalique.

8. Le composant selon une ou plusieurs des revendications 2 à 6, dans lequel le dérivé électro-donneur est choisi parmi les 1,3-diéthers de formule :

$$R^I \diagdown C \diagup CH_2\text{-}OR^{III}$$
$$R^{II} \diagup C \diagdown CH_2\text{-}OR^{IV}$$
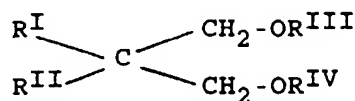
dans laquelle

R^I et R^{II}, identiques ou différents l'un de l'autre, sont des radicaux alkyles, cycloalkyles ou aryles comportant 1 à 18 atomes de carbone,
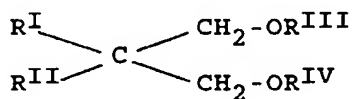R^{II} et R^{IV}, identiques ou différents, sont des radicaux alkyles comprenant 1 à 4 atomes de carbone.

9. . Le composant selon l'une ou plusieurs des revendications précédentes dans lequel le dérivé de titane est présent en une proportion comprise entre 0,5 et 10% en poids, exprimée en Ti métallique.

10. Un catalyseur de polymérisation des oléfines, comprenant le produit de la réaction entre un composant catalytique selon la revendication 1 et un dérivé Altrialkyle.

11. Le catalyseur selon la revendication 10 dans lequel on utilise pour la préparation du catalyseur un dérivé électro-donneur (donneur externe).

12. Le catalyseur selon la revendication 11, dans lequel le composant catalytique solide comprend un électro-donneur choisi parmi les esters d'alkyle, de cycloalkyle et d'aryle de l'acide phtalique et le donneur externe est choisi parmi les dérivés de silicium répondant la formule R$_1$ R$_2$Si(OR)$_2$, où R$_1$ et R$_2$, identiques ou différents, sont des radicaux alkyles, cycloalkyles ou aryles comportant 1 à 18 atomes de carbone et R est un radical alkyle comportant 1 à 4 atomes de carbone.

13. Le catalyseur selon la revendication 11, dans lequel le donneur externe est choisi parmi les 1,3-diéthers de formule :

$$R^I \diagdown \quad \diagup CH_2-OR^{III}$$
$$C$$
$$R^{II} \diagup \quad \diagdown CH_2-OR^{IV}$$

dans laquelle

R^I et R^{II}, identiques ou différents l'un de l'autre, sont des radicaux alkyles, cycloalkyles ou aryles comportant 1 à 18 atomes de carbone et
R^{II} et R^{IV}, identiques ou différents, sont des radicaux alkyle comportant 1 à 4 atomes de carbone.

14. Un adduct MgCl$_2$/alcool ROH où R est un radical alkyle, cycloalkyle ou alkylaryle comportant 1 à 12 atomes de carbone, convenant à la préparation du composant catalytique selon une ou plusieurs des revendications 1 à 9, comportant de 0,2 à 2 moles d'alcool par mole de MgCl$_2$, et présentant une surface spécifique comprise entre 10 et 50 m^2/g, une porosité (au mercure) de 0,6 à 2,5 cm^3/g et une distribution de volume de pore telle qu'au moins 50% de pores ont un diamètre supérieur à 10 000 Å.

15. Un procédé de préparation du composant catalytique selon l'une ou plusieurs des revendications précédentes 1 à 9, comprenant la réaction

1) d'un adduct MgCl$_2$/alcool ROH selon la revendication 14 avec
2) un dérivé de titane contenant au moins une liaison halogène-titane.